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ION MIXING OF Ti/C AND Fe/C BILAYERS

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ABSTRACT

Bilayer samples of Ti/C and Fe/C have been ion beam mixed with 400 keV Xe ions to a dose of 1×10^{16} ions/cm². Mixing experiments were performed at 77, 300, 573, and 723 K. The transition between the temperature independent and temperature dependent mixing occurred between 300 and 573 K in Fe/C samples and between 573 and 723 K in Ti/C sample. In the temperature independent mixing regime mixing is reasonably well explained by a thermodynamic model of ion mixing while at higher temperatures a radiation enhanced diffusion mechanism is evident.

INTRODUCTION

The ion beam mixing of Ti/C and Fe/C thin film bilayers have been studied as a function of temperature to test the applicability of the thermodynamic model of ion beam mixing [1,2] in a metal/metalloid system. These experiments are an extension of a set of experiments which examined mixing and phase formation in the Fe/C and Ti/C systems for irradiations at room temperature (~300 K) [3].

EXPERIMENT

Bilayer metal/C samples on SiO₂ substrates were produced by the sequential electron beam deposition of a 900 Å metal layer (Fe or Ti) followed by 900 Å of C. For Fe/C samples a small amount of Ti was first deposited to facilitate adhesion of Fe to SiO₂. The thickness of the as-deposited layers was measured using Rutherford backscattering spectroscopy (RBS). Backscattering was carried out using 2.3 MeV alpha particles with backscattered particles detected at 160° and the sample tilted 45° toward the detector.

The bilayered samples were ion beam mixed in a base vacuum of 8×10^{-7} torr, at 77, 300, 573, and 723 K using 400 keV Xe⁺⁺ ions. This energy results in a range of 1400 Å in the Ti/C case and a range of 1250 Å in the Fe/C case [4]. A Xe⁺⁺ current density of 2 μA/cm² and an ion mixing dose of 1×10^{16} ions/cm² was used for all irradiations.

RESULTS AND DISCUSSION

Rutherford backscattering analysis was used to examine the ion induced reaction at the Fe/C and Ti/C interface. The number of metal atoms in the carbon layer was used as a measure of the mixing. Backscattering data, reported in Fig. 1, clearly shows that mixing is temperature sensitive in both systems. Plotting the number of metal atoms reacted after an irradiation of 1×10^{16} Xe/cm² as a function of 1/T produces curves, Fig. 2., which indicate that both Ti/C and Fe/C possess a temperature independent

regime at low temperatures and a strongly temperature dependent regime at higher temperatures. The transition temperature between these two regimes occurs between 300 and 573 K for Fe/C and between 573 and 723 K for Ti/C. At 77 K mixing in the Ti/C system exceeded Fe/C mixing by a factor of 1.1 while at the maximum temperature studied, 723 K, mixing in the Fe/C system exceeded Ti/C mixing by a factor of 3.4.

The amount of ion mixing expected at low temperatures in metallic bilayer system has been reasonably well predicted by the thermodynamic model of ion-beam mixing proposed by Johnson and co-workers [1,2]. In this model ion mixing is influenced by the attractive or repulsive thermodynamic forces operating in the alloy system (the heat of mixing or free energy of mixing), the cohesive energy of the alloy, and the amount of damage energy deposited by the ion beam at the interface.

Experimental mixing data from metal bilayers in the temperature independent regime where collisional mixing dominates were found to be in good agreement with the expression [1]

$$Q = \frac{K_1 E^2}{\rho^{5/3} \Delta H_{coh}^2} (1 + K_2 \frac{\Delta H_{mix}}{\Delta H_{coh}}) \quad (1)$$

where Q is a measure of intermixing, ΔH_{mix} is the heat of mixing, ΔH_{coh} is the cohesive energy, ϵ is the energy deposited per unit path length, ρ is the average atomic density, and K_1 and K_2 are fitting constants which were found to be 0.037 Å and 27 respectively.

For the present experimental conditions ϵ was determined to be 152 and 115 eV/Å for Fe/C and Ti/C respectively from the Monte Carlo simulation TRIM [5]. To obtain a reasonable value for the thermodynamic parameter ΔH_{mix} , the free energy diagrams for the Fe/C and Ti/C alloy system were constructed at 100 K from the data of Kaufman and Nesor [6,7], Figs. 3 and 4. We have taken the liquid curve (L) at 100 K as the amorphous state. The dashed line in each of the diagrams represents the free energy state of the as-deposited metal/C bilayers. The states of the end points, hcp-Ti, bcc-Fe, and amorphous-C, were determined by transmission electron microscopy examination of the as-deposited films. The difference in free energy between the as-deposited and the intermetallic compound state at the compositions Fe₃C and TiC were substituted for ΔH_{mix} in Equation 1. The cohesive energy was calculated according to the expression [1] $\Delta H_{coh} = 1/2 (H_M + H_C) + \Delta H_{mix}$ where H_M and H_C are the cohesive energy of pure metal and carbon respectively [8]. Values used in Equation 1 are presented in Table I.

TABLE I. Data for Equation 1

M/C	ϵ (eV/Å)	$\rho^{5/3}$ (at/Å ³)	ΔH_{coh} (eV/at)	$\Delta G(100K)$ (eV/at)	$(Q_{M/C})_{model}$ (Å ⁴)
Ti/C	115	9.4×10^{-2}	-7.1	-1.5	2.9×10^3
Fe/C	152	2.5×10^{-2}	-5.9	-0.2	2.0×10^3

Using Equation 1 and the data presented in Table I, the thermodynamic model of ion mixing predicts that mixing between Ti and C should be 1.5

greater than mixing between Fe and C. Experimentally (Fig. 2) Ti/C mixing exceeds Fe/C mixing by a factor of 1.1 and 1.4 at 77 K and 300 K respectively which is in reasonable agreement with the model. It is worthwhile to note that the use of published ΔH_{mix} values [6] in Equation 1 without making energy corrections for the differences between standard states and the actual states in our as deposited films results in a 200% error between calculation and experiment.

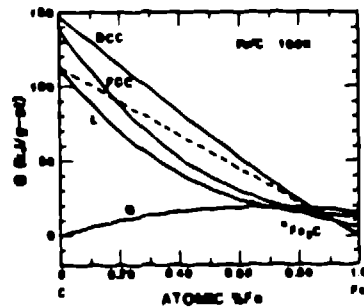
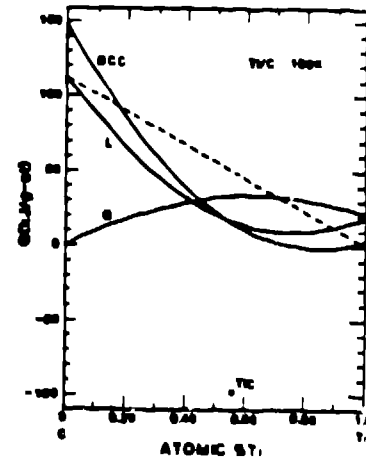


Fig. 3. Free energy curves of the Fe/C alloy system constructed from the data of Ref. 6 and 7. The as-deposited state (dashed line) was determined to be bcc-Fe and amorphous-C.

Fig. 4. Free energy curves of the Ti/C alloy system constructed from the data of Ref. 6 and 7. The as-deposited state (dashed line) was determined to be hcp-Ti and amorphous-C.



Clearly, as expected, at higher temperatures experimental mixing data is not well explained by Equation 1; at 723 K Fe/C mixing exceeds Ti/C mixing by a factor of 3.4. This mixing trend is positively correlated with carbon diffusion in Fe and Ti as well as carbon diffusion in Fe₃C and TiC. At 723 K and the diffusivity of C in hcp-Ti and bcc-Fe is 3.5×10^{-13} and 1.7×10^{-8} cm²/sec respectively [10] and in TiC and Fe₃C it is 1×10^{-29} and 5×10^{-16} cm²/sec respectively [11,12]. Hence the slope changes at higher temperatures shown in Fig. 2 supports a radiation enhanced diffusion mechanism.

In summary, ion mixing is temperature independent at 300 K or lower for Fe/C and at 573 K or lower in Ti/C, and is reasonable agreement with the thermodynamic model of Johnson and co-workers [1,2]. At higher temperatures a radiation enhanced diffusion mechanism is clearly evident which is correlated with the respective C diffusivities.



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